FLUID SYNTHESIS AND STRUCTURE OF NOVEL BORON NITRIDE POLYMORPHE - HYPERDIAMOND FULBORENITE HDF-B12N12 (E-PHASE)

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Keywords: BN, polymorph, E-phase, fulboren, fluid synthesis

Introduction

For boron nitride as being the isomorphic analog of carbon several polymorph phases, intermediate in density between graphite-like g-BN and cubic c-BN, have been discovered [1-7].Batsanov was the first who have synthesized a novel BN polymorph named E(Explosion)-phase by shock compression of turbostratic t-BN [1-3] . Its elementary cell was proposed to be rhombohedral with the parameters a=0.72 nm, b=0.81 nm, c=1.89 nm [2]. Akashi have obtained a novel BN phase by multiple shock compression identifying its unit cell as face centered lattice with parameter a=0.8405 nm [4]. Sokolovski, Olszyna et al. have synthesized the E-phase by different techniques notably at normal pressure [5,6]. Wang et al. have obtained E-phase nanocrystals at g-BN/acetone interface by pulsed laser irradiation [7].

In this work a novel BN polymorph for a first time was obtained by supercritical fluid synthesis, the XRD pattern and IR spectra of which are close to E-phase. Its structure was suggested to be hyperdiamond fulborenite HDF-$B_{12}N_{12}$ that confirmed by XRD analysis. It is novel faujasite on base of BN.

Results

Synthesis was carried out on high pressure gazostat at intermediate pressure (P~200MPa) and temperature (T<1000C) in different atmospheres (He, H_2O, N_2, Ar). At the conditions the gaze transforms in a supercritical fluid becoming an effective catalyst which easy penetrates in crystalline lattice due to its low viscosity. Samples were characterized by SEM, TEM, XRD, IR, Raman, and EPR techniques. In table 1 XRD results are presented.

In spite of some discrepancy one can to conclude that: 1) number of lines in our samples relate to unconventional BN polymorph; 2) this lines are in satisfactory correlation with the lines distinguishing for E-phase; 3) number of lines calculated for HDF-$B_{12}N_{12}$ are in good agreement with experimental ones for E-phase.

The IR spectra of our samples in spite of some discrepancy are closed to the lines peculiar for both the E-phase, namely, (450, 550, 700, 800, 940, 1030, 1110, 1200, 1260, 1400, 1650 cm^{-1}) [1] and the nanocrystalline BN (649, 699, 783, 883, 927, 1026, 1104, 1195, 1252, 2260, 3217, 3376 cm^{-1}) [7] . Two common lines 927 cm^{-1} (960 cm^{-1}) and 1250 cm^{-1} are the most peculiar for E-phase [1,7].

Raman and EPR spectra confirm the presence of novel phase in turn.

To resolve unknown so far E-phase structure we have considered the number of potential sc, fcc, bcc, hcp, sphalerite and wurtzite lattices , named as fulborenites [8], with fulborene molecules B12N12 and B24N24 in it vertexes. Among them only the diamond type lattice called us as hyperdiamond fulborenite HDF-B12N12 [8] (fig.1) gives the satisfactory agreement between experimental (A=1.114 nm, ρ=2.5- 2.6 g/cm3) [3] and calculated (A=1.152 nm, ρ=2.59 g/cm3) values of lattice parameter and density under a bond length aBN=0.145 nm.

Table 1. Some XRD interplane distances for E-phase [3,4,5,7] in comparison with our experimental samples (1-4)) and suggested HDF-B12N12 structure.

[3]	[5]	[7]	[4]	1	2	3	4	HDF-$B_{12}N_{12}$
-	-	-	-	8.04	8.84	12.20	10.40	10.88
6.28	-	6.146	-	6.03	6.03	5.95	5.98	6.280
4.85	5.03	-	4.854	5.19	-	4.58		4.864
4.25	4.27	-	4.330	-	4.58		4.53	4.441
3.85	3.86	3.86	-	3.95	3.90		4.14	3.846
3.54	3.56		-	3.51	3.51	3.49	3.52	3.626
3.04	3.20	3.189	-	3.19	3.18	3.18	3.16	3.140
2.983	-	2.981	2.973	3.03	3.01			3.017
2.784	2.97	-	-	2.91	2.92	2.91	2.93	2.907
2.686	2.64	2.689	-	2.72	2.70			2.719
2.567	-	2.57	2.536	2.54	2.53	2.54		2.564
2.430	2.41	2.428	-	-	-			2.432
2.298		-	-	2.29	-	2.28		2.374
2.201	2.21	2.239	-	2.24	-	2.24	2.23	2.220
2.076	2.04	-	-	2.08	2.09	2.09	2.10	2.093
1.955	1.99	-	-	1.933	-			1.923
1.901	-	-	-	-	1.907	1.903	1.845	1.893
1.769	-	-	-	1.752	-			1.764
1.696	1.68	-	1.716	1.685	-	1.681		1.720

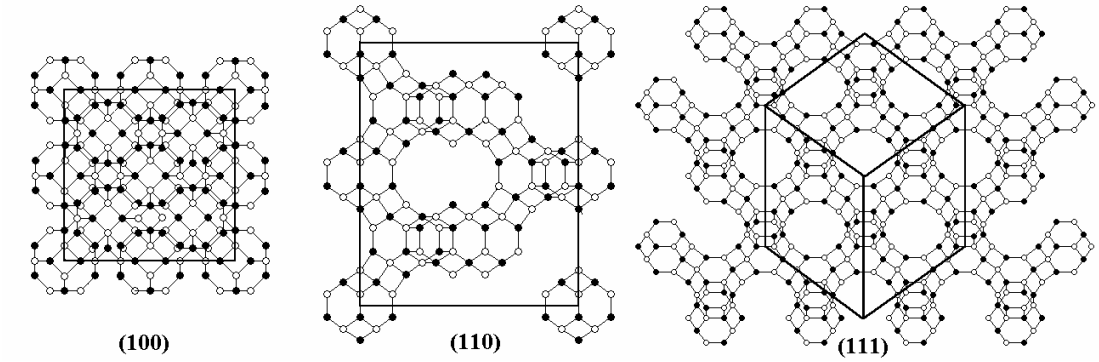

Fig.1. Fragments of elementary cell in (100), (110), and (111) planes of hyperdiamond fulborenite HDF-$B_{12}N_{12}$ suggested as E-phase. It is diamond type lattice with fulborene $B_{12}N_{12}$ in its vertexes copolymerized by hexagonal faces with alternated B-N atoms.

Acknowledgement

This research was made possible in part by Award UE2-2456-KV-02 of U.S. CRDF.

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